Development of Antimony Free Stereolithography Resin For Investment Casting

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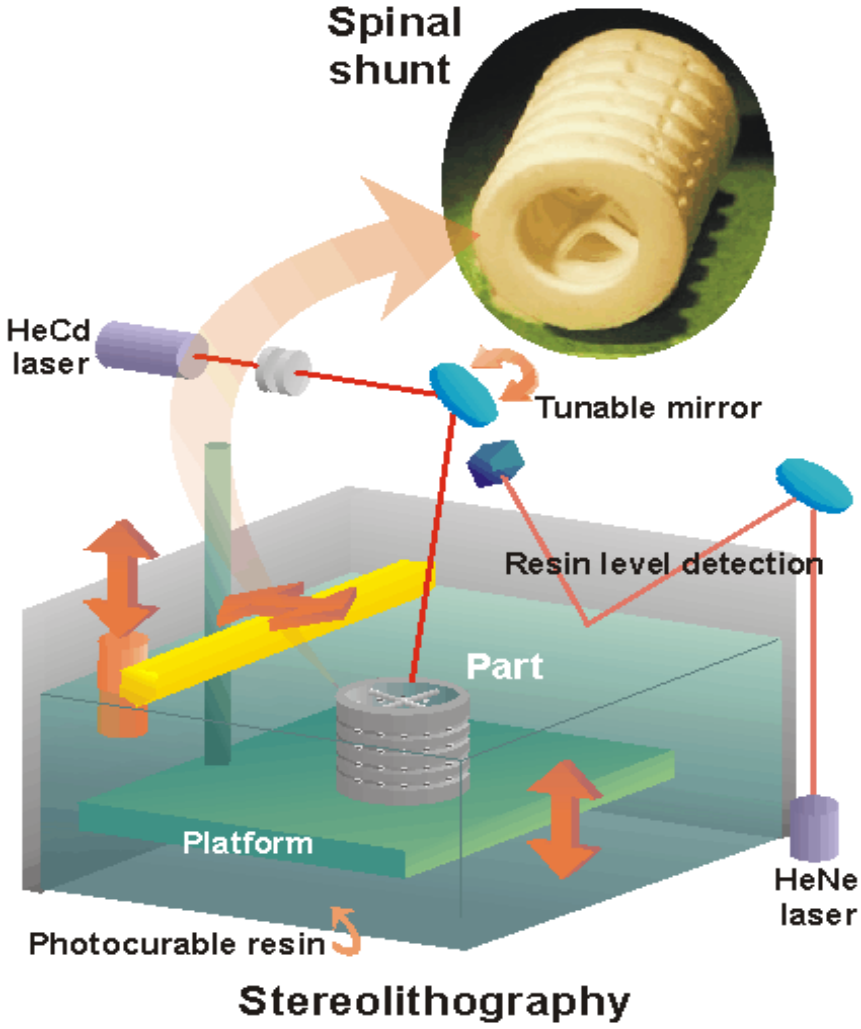
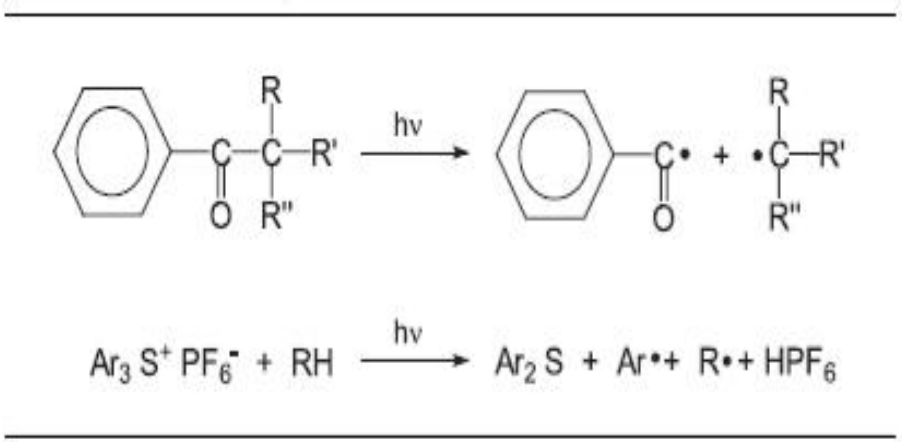
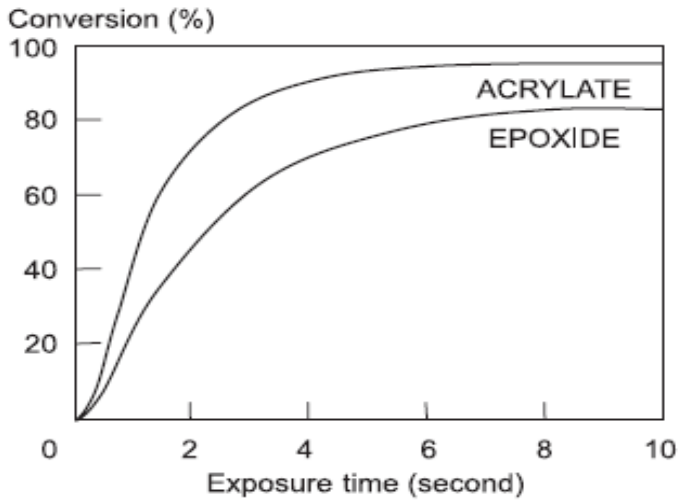
OUTLINE

1) Stereolithography fundamentals
2) Direct casting fundamental
3) Development of antimony free formulation
4) Application Sb free resin for investment casting

Stereolithography Fundamentals







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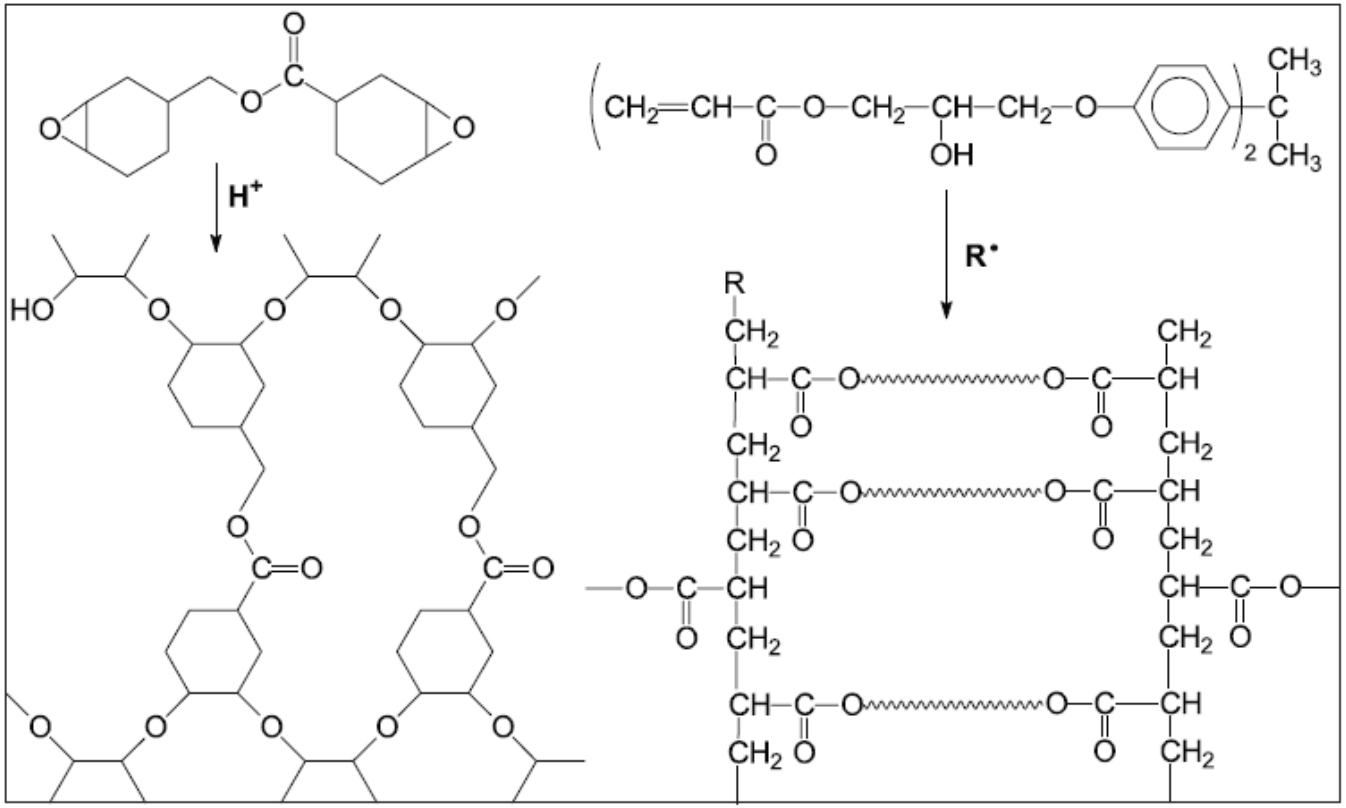
Photopolymerization for Stereolithography



Cationic photopolymerization **Radical Photopolymerization**

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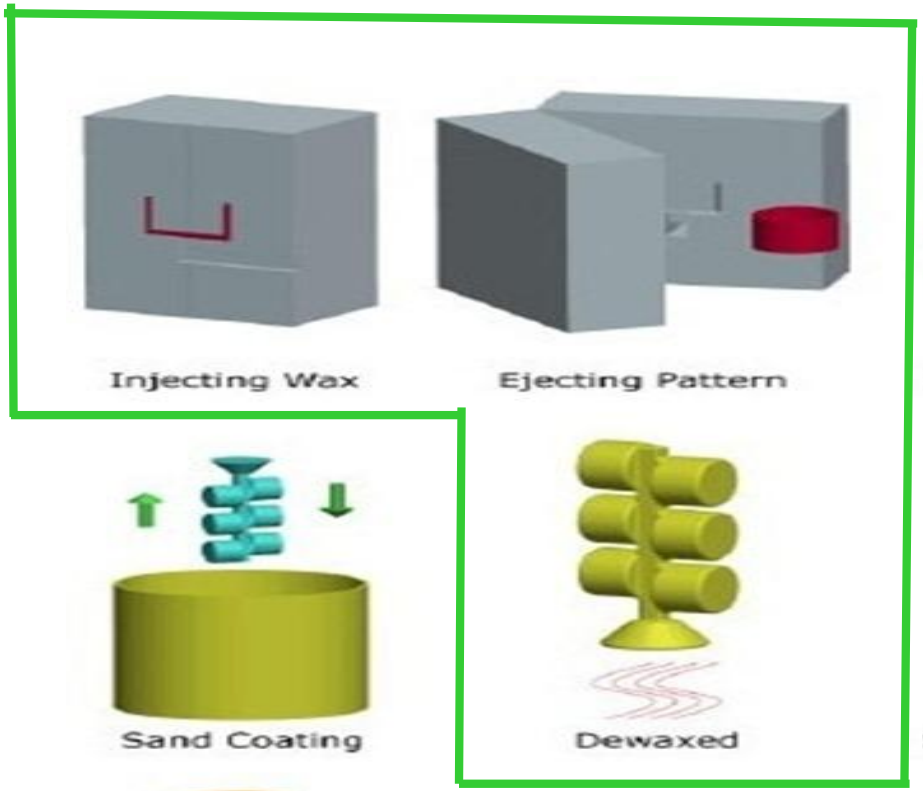
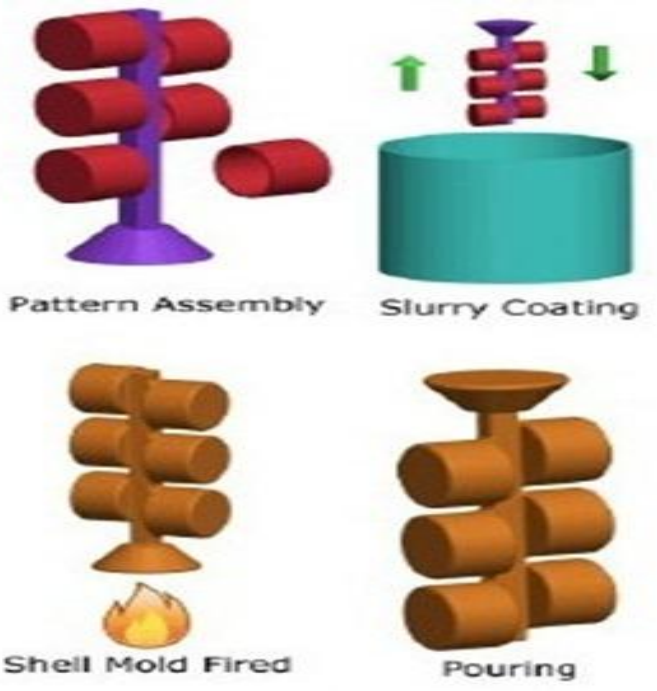
Investment Casting Procedure





Direct Casting

- no mold, no wax tool
- save time and cost

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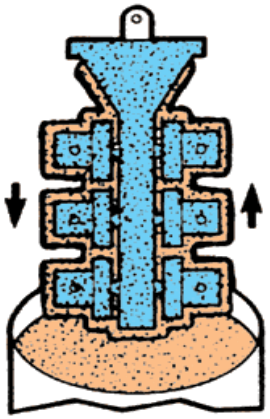
Direct Casting by Stereolithography

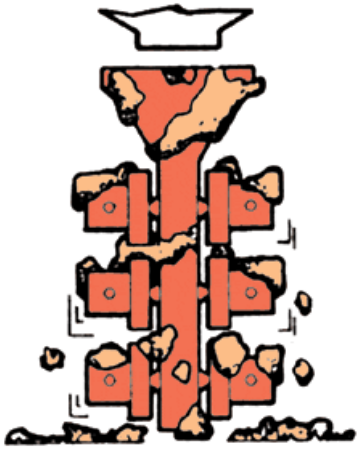
Assemble SL parts



Coat ceramic slurry

Burnout SL parts

Pour metal into ceramic mould



Remove ceramic shell

Casted metal parts

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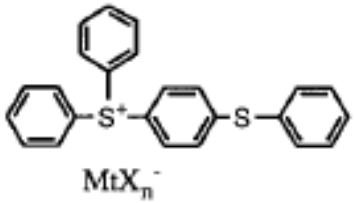
Surface Defect of Casted Part

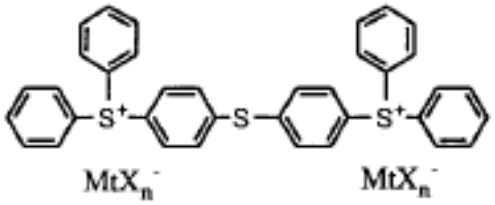
1) Ash residue: $Ar_3S^+ SbF_6^- + O_2 \xrightarrow{\Delta} Sb_2O_3 + \text{Others}$

2) Metal alloy degradation: $3\ SbF_6^- + 5\ Al \xrightarrow{\Delta} 3\ Sb + 5\ AlF_3 + 3\ F^-$

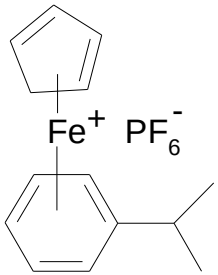
M. Ponikvar, *Talanta.* **2002**, *58*, 803

Commercially available Sb free photoinitiator



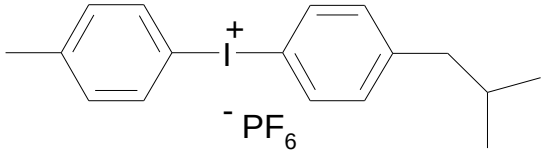


MtXn = SbF_6
the common initiator in SL resins
MtXn = PF_6
slower cure speed and
insufficient green strength



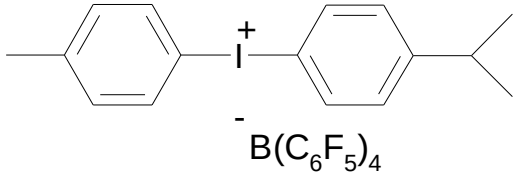
Irgacure 261

metal presence
Yellow color
Long wavelength abs.
Insufficient green strength



Irgacure 250

Slow curing
Short wavelength abs.
Insufficient green strength



Rhodorsil 2074

Fast curing
Short wavelength abs.
Excellent green strength

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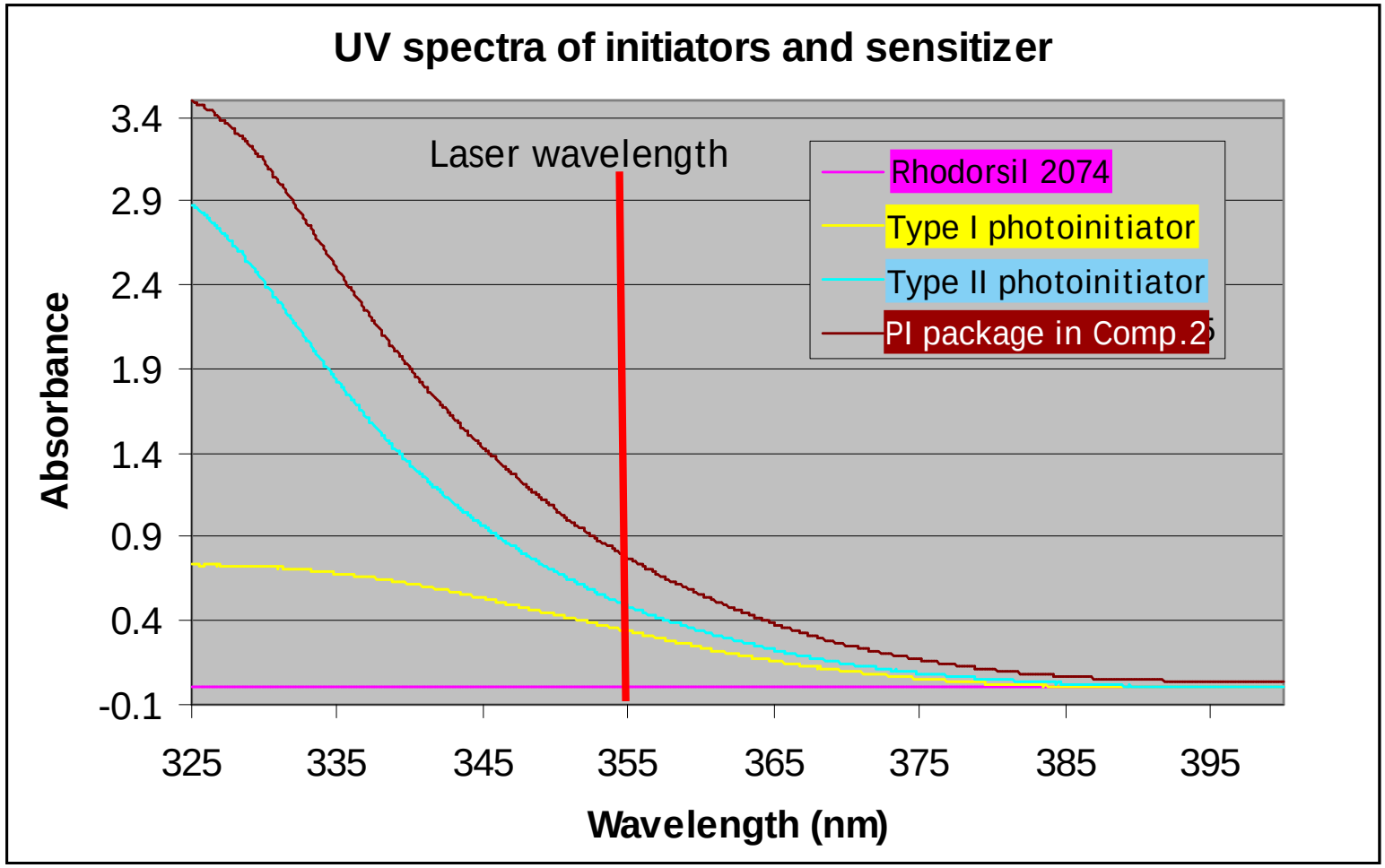
Photoinitiator Package



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Run-away Reaction

Sunlight Cure- Petri-dish top, Bottle Side View

Run-away reaction

Resin became brown, black or even smoking under actinic radiation due to exothermal

$(C_6H_5)_3S^+AsF_6^-$
($E^{red}_{1/2}$ = -1.2 eV vs. SCE)
$(C_6H_5)_2I^+AsF_6^-$
($E^{red}_{1/2}$ = -0.2 eV vs. SCE)

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Technical approaches to stabilization of antimony free resins

Light absorbers
Light blockers

Slow down both acrylate and epoxy curing speed

(In)organic bases

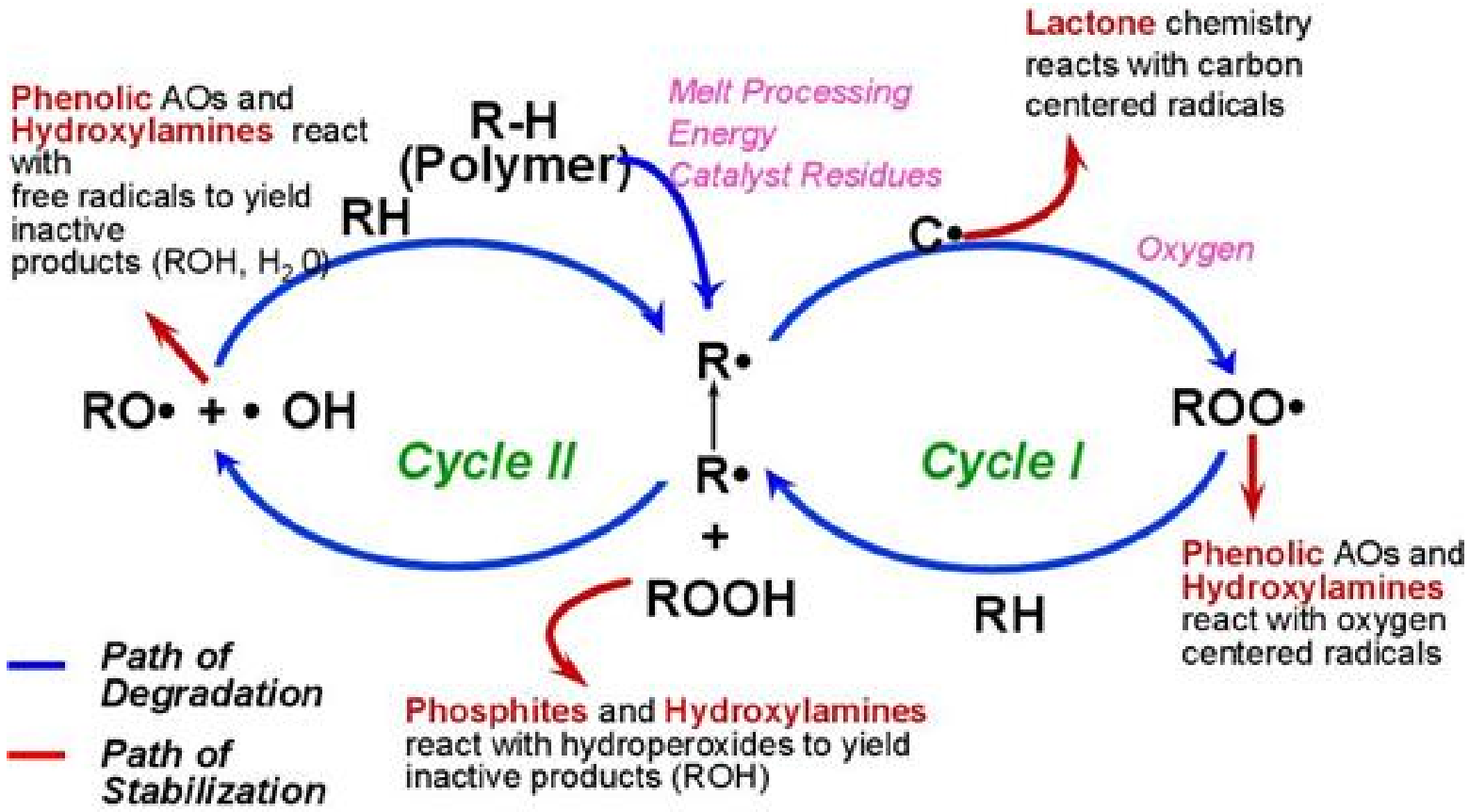
Slow down epoxy curing speed

Slow down acrylate curing speed

Radical scavengers

J. V. Crivello, *J. Polym. Sci. A: Polym. Chem.* **1999**, *37*, 4241
S.R. Kerr, *U.S. Patent 5,973,020*, Oct 26, **1999**

Antioxidant as radical scavenger



Thermal degradation controlled by AOs and HALS
HALS could inhibit epoxy curing

Exposure stability test on base compositions w/o antioxidant1

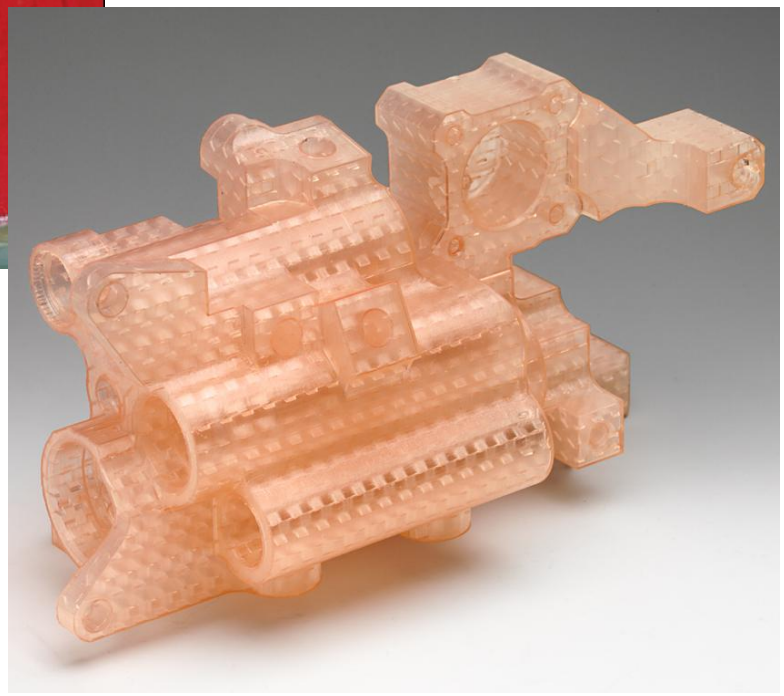
Base Composition	Comp. 1	Ex. 01	Comp.2	Ex. 02
Epoxide A	88.9	88.9		
Mixture of Epoxides			86.74	86.74
Epoxide B	10	10		
Rhodorsil 2074	0.9	0.9	1	1
Acrylate			6	6
Type II photoinitiator	0.2	0.2	0.16	0.16
Type I photoinitiator			5	5
Additives			1.007	1.007
Antioxidant 1		0.1		0.1
Exposure stability (20g sample in petri-dish for PCA)				
Browning Time (mins exposure)	2.6	4.7	<10	>10

Comparative example 2 and their mixture with different concentration of antioxidants

Base Composition	**Ex. 03**	**Ex.04**	**Ex.05**	**Ex. 06**
Antioxidant 1			0.05	0.075
Antioxidant 2	0.1	0.05	0.05	
Green strength (cured strips)	Poor	Better	Better	Better
E10 (mJ/cm2)		27.3	27.23	45.49
Dp (mm)		0.30	0.29	0.26
Exposure stability (20g sample in petri-dish for PCA)	Pass	Pass	Pass	Pass
Exposure stability (15 g sample in petri-dish for PCA)	Pass	Pass	Fail	Pass

DSM Somos® antimony free SL resin

QuickCast™ pattern
built from PhrotoCast™19120



DSM Somos® 19120 reduced
the residual ash to be less than 0.01%,
versus 0.3% for DSM Somos® 11120

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Summary

Antimony Free Stereolithography Resin:

1. PI Package: Iodonium borate/type I&II photoinitiator/Antioxidant
2. Run-away reaction was controlled
3. Minimum ash content
4. Better surface quality for casting parts
5. More environmentally friendly SL resin (medical modeling)